

Solid-state interdiffusion reactions in Ni/Ti and Ni/Zr multilayered thin films

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We have performed a comparative transmission electron microscopy study of solid-state interdiffusion reactions in multilayered Ni/Zr and Ni/Ti thin films. The Ni-Zr reaction product was amorphous while the Ni-Ti reaction product was a simple intermetallic compound. Because thermodynamic and chemical properties of these two alloy systems are similar, we suggest kinetic origins for this difference in reaction product.

The growing technological importance of thin-film materials has led to many recent studies of phase transformation at interfaces in thin-film diffusion couples.¹ In the early stages of interdiffusion, the kinetics of nucleation and growth for the different possible reaction products can favor the formation of nonequilibrium phases. Recently, the formation of an amorphous phase by low-temperature solid-state interdiffusion in both metal-metal and metal-semiconductor crystalline thin-film diffusion couples was experimentally demonstrated.^{2,3} The formation of amorphous phases during such solid-state reactions seems now to be rather common in metal-metal systems.⁴ Thermodynamics favors the formation of intermetallic compounds rather than an amorphous phase, so the kinetics of nucleation and growth must be responsible for the formation of amorphous phases during solid-state reactions. Here we report results of a comparative transmission electron microscopy (TEM) study of solid-state reactions in Ni/Zr and Ni/Ti diffusion couples, and we assess kinetic factors which may influence the phases formed during such processes.

Enthalpy of formation can be used as a measure of the thermodynamic driving force for the formation of various phases at low temperatures. Experimental studies of Ni-Zr systems reported heats of formation of amorphous Ni-Zr alloys near the equiatomic composition of 35–40 kJ/mol, whereas the heats of formation for Ni-Zr compounds are only a few kJ/mol larger.⁵ The thermochemical data available for the Ni-Ti system indicate that heats of formation of various Ni-Ti compounds are around 35 kJ/mol.⁶ Miedema *et al.*'s heats of formation for NiZr and NiTi intermetallics are also very similar.⁷ We chose to compare the systems Ni-Zr and Ni-Ti in the present work because the thermodynamic driving forces for the formation of both the amorphous and the crystalline phases in both alloy systems are so similar.

Multilayers of Ni/Zr and Ni/Ti were prepared by electron beam evaporation with a base pressure about 10^{-8} Torr. The chamber pressure during evaporation stayed below 10^{-7} Torr. For comparison, thin films were also fabricated by a dc magnetron sputtering technique.⁵ Alternating 100-Å layers of Ni and Zr (or Ni and Ti) were deposited onto cleaved NaCl substrates. Subsequent heat treatments of both Ni/Zr and Ni/Ti multilayers were carried out in a vacuum furnace at 250 and at 300 °C with pressure less than 5×10^{-7} Torr. The foils were then floated off their substrates

in de-ionized water, cleaned in ethanol, and mounted on copper grids. These specimens were examined in plane-view geometry with a Philips EM 430 transmission electron microscope operated at 300 kV.

Selected area diffraction patterns of unreacted Ni/Zr and Ni/Ti thin films are shown in Fig. 1. Sharp rings characteristic of polycrystalline materials are observed in both cases. All rings were indexed to the diffraction patterns of the elemental metals Ni, Zr, or Ti. The extent of interfacial reaction during deposition is apparently insignificant. Small-angle x-ray diffraction from Ni/Ti multilayers showed five to six low angle satellites due to the composition modulation, indicating sharp Ni/Ti interfaces.

Figure 2(a) shows a selected area diffraction pattern from a Ni/Zr film annealed at 250 °C for 5 h. It is evident that diffuse bands characteristic of an amorphous phase have appeared, but some sharp rings from unreacted metals are still present, indicating an incomplete reaction. Bright field and dark field micrographs taken from the first diffuse band show the typical "grey and fine" contrast characteristic of amorphous phases [see Fig. 2(b)]. This is consistent with previous results obtained from x-ray diffraction studies at various low temperatures from 250 to 320 °C.⁸

Figure 3(a) shows a selected area diffraction pattern

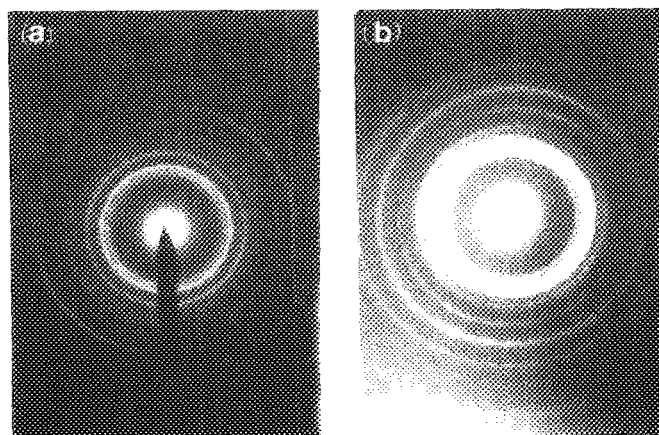


FIG. 1. Selected area diffraction patterns of unreacted (a) Ni/Zr, (b) Ni/Ti multilayered thin films prepared by electron beam evaporation. Each individual layer is 100 Å in thickness. Total thicknesses are (a) 400 Å of Zr and 300 Å of Ni (b) 500 Å of Ti and 400 Å of Ni.

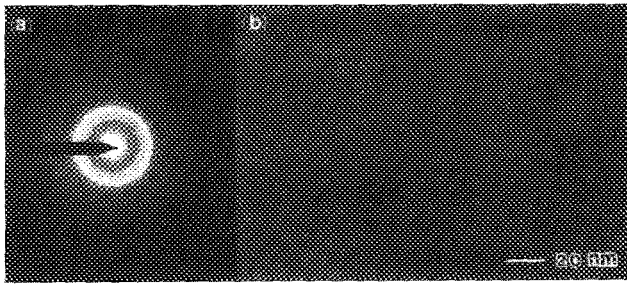


FIG. 2. Ni/Zr multilayered thin film reacted at 250 °C for 5 h: (a) selected area diffraction pattern; (b) bright field micrograph.

from a Ni/Ti film annealed at 250 °C for 10 h. This diffraction pattern did not contain the diffuse bands characteristic of an amorphous phase. In addition to rings corresponding to unreacted metals, new rings appeared. These new rings are close to those of a $B2$ (CsCl type) intermetallic compound of NiTi. This identification is not definitive; slightly different heat treatments resulted in slight differences in these diffraction rings. We believe this is because equiatomic NiTi alloys are “shape memory alloys” which undergo a structural phase transformation between room temperature and 300 °C.⁹ Nevertheless, the lack of closely spaced diffraction rings in Fig. 3(a) indicates a small and simple unit cell like that of the $B2$ structure. Figures 3(b) and 3(c) show a bright field micrograph and a dark field micrograph taken from the first strong diffraction ring of this intermetallic NiTi. It is clear that crystallites of NiTi smaller than 100 Å in size are formed during annealing. The diameter of these crystallites is much smaller than the 900 Å total thickness of the thin film. It seems that these crystallites nucleated profusely at the Ni/Ti interfaces and grew until neighboring crystallites were encountered. The diffraction pattern [Fig. 3(a)] shows some fourfold orientational symmetry. This could originate from the fourfold symmetry of the (100) NaCl substrate surface, which may influence the orientation of the deposited Ni and Ti layers, to which the NiTi crystallites are crystallographically related. This is a point which requires further study. The same NiTi intermetallic compound was observed in sputtered deposited Ni/Ti multilayers after reaction at the same temperature. However, the texture of the NiTi crystallites differed from that of the evaporated multilayers, and no fourfold orientational symmetry was observed. Similar results were observed in Ni/Ti multilayers reacted at 300 °C.

Our key observation, however, is that in spite of the similar thermodynamic driving forces, completely different phases form during solid-state reaction of Ni/Ti and Ni/Zr multilayers. The Ni/Ti multilayers formed a simple intermetallic compound and the Ni/Zr multilayers formed an amorphous alloy. This difference may stem from the difference in structure of the equilibrium intermetallic compounds of Ni-Zr and Ni-Ti. All Ni-Zr intermetallic compounds near the equiatomic composition possess fairly complicated crystal structures with unit cell volumes greater than 100 cubic angstroms.¹⁰ Alternatively, the intermetallic compound for NiTi has a simple unit cell, and this is indeed

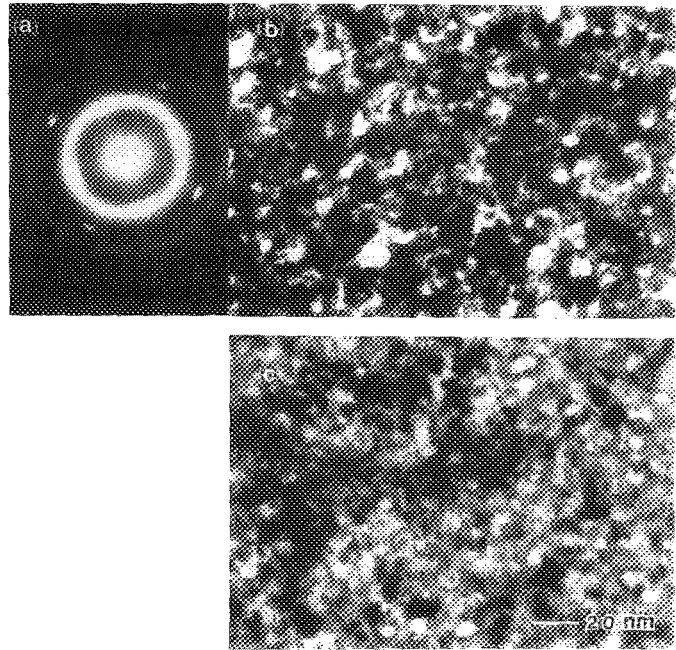


FIG. 3. Ni/Ti multilayered thin film reacted at 250 °C for 10 h: (a) selected area diffraction pattern; (b) dark field micrograph; (c) bright field micrograph.

the observed product of our low-temperature interdiffusion reaction. A few atomic movements suffice to form a critical nucleus of the NiTi intermetallic compound while formation of the Ni-Zr compounds requires correlated movements of many atoms for both nucleation and growth. So given a specific thermodynamic driving force for mixing, the tendency to form a particular product phase could depend on the spatial range of the atom movements required for its formation.

Once an amorphous phase nucleates, its growth requires interdiffusion through the amorphous phase. If this process is slow, the amorphous/crystalline interfaces would advance more slowly, making more time available for nucleation of the competing intermetallic compounds at these interfaces. Although there are data for interdiffusion in amorphous Ni-Zr,^{8,11} such data for amorphous Ni-Ti are lacking. In the absence of such data, we note that Ni diffusion through amorphous Ni-Zr could be faster because of the larger difference of atomic radii of the two constituents. The diffusion of Ni in crystalline Zr is known to be faster than in crystalline Ti.¹² A rapid diffusion of Ni through the amorphous Ni-Zr reduces the time available for the formation of intermetallic compounds, but the complicated Ni-Zr intermetallic compounds require a substantial amount of time to form. Hence kinetic factors favor the formation of an amorphous phase in Ni-Zr, but these factors are less significant for Ni-Ti.

In summary, we have carried out a comparative TEM study of solid-state interdiffusion reactions in multilayered Ni/Zr and Ni/Ti thin films. These two thermodynamically and chemically similar systems develop completely different reaction products: an intermetallic compound for Ni-Ti and an amorphous alloy for Ni-Zr. We suggest that differences in the relative ease of nucleation and differences in diffusivities are factors which determine the formation of the particular phases in these two alloy systems.

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